

(12) UK Patent Application (19) GB (11) 2 356 258 (13) A

(43) Date of A Publication 16.05.2001

(21) Application No 0027168.4

(22) Date of Filing 07.11.2000

(30) Priority Data

(31) 11318116	(32) 09.11.1999	(33) JP
(31) 12029159	(32) 07.02.2000	
(31) 12029156	(32) 07.02.2000	
(31) 12119397	(32) 20.04.2000	

(51) INT CL<sup>7</sup>

G03F 7/004 7/039

(52) UK CL (Edition S )

G2C CRPC C1G1 C1H

(56) Documents Cited

JP 100239846 A US 5665527 A US 5660969 A

(58) Field of Search

UK CL (Edition R ) G2C CRM CRPC

INT CL<sup>7</sup> G03F 7/004 7/038 7/039

ONLINE: EPODOC, JAPIO, WPI

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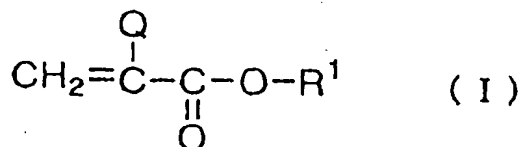
(54) Abstract Title

Chemical amplification type resist composition

(57) A chemical amplification type resist composition comprises

a radiation sensitive compound; and

a binder resin which is soluble in alkali by itself or becomes soluble in alkali by a chemical change caused by the action of the radiation sensitive compound after irradiation, and has a polymerization unit derived from a monomer of formula (I):



wherein Q represents hydrogen, methyl or a fluoroalkyl having 1 to 4 carbon atoms; R<sup>1</sup> represents an alkyl having 1 to 14 carbon atoms; provided that at least one of Q and R<sup>1</sup> has at least one fluorine atom.

The composition exhibits a high transmittance in light exposure using a light source having a wavelength of 170 nm or less and a high resolution in KrF or ArF light exposure, and has a sufficient contrast.

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## CHEMICAL AMPLIFICATION TYPE RESIST COMPOSITION

## BACKGROUND OF THE INVENTION

The present invention relates to a chemical  
5 amplification type resist composition usable in the fine  
processing of semiconductors.

The fine processing of semiconductors has usually been  
performed by adopting the lithography process using a resist  
composition. In the lithography process, as indicated by the  
10 Rayleigh's equation for limit of diffraction, it principally  
becomes more possible to improve resolution with shortening  
wavelength for exposure. Wavelength of light source for  
lithography process in the production of semiconductors has  
been becoming shorter and shorter year by year, in such order  
15 as g-ray at a wavelength of 436 nm, i-ray at a wavelength of  
365 nm, KrF excimer laser at a wavelength of 248 nm and ArF eximer  
laser at a wavelength of 193 nm. Furthermore, F2 excimer laser  
at a wavelength of 157 is attracting attention as a next  
generation of the light source. For exposure with KrF excimer  
20 laser or that with ArF excimer laser, so-called chemical  
amplification type resists utilizing a catalytic action of an  
acid generated by light exposure have frequently been used  
because of their excellent sensitivity. It is also considered  
that chemical amplification type resists will be used for  
25 exposure with F2 excimer laser because of their excellent  
sensitivity.

Conventionally, polyvinylphenol resins have been used  
as resists for exposure with KrF excimer laser. As resists for

exposure with ArF excimer laser, resins without an aromatic ring and, instead, having an alicyclic ring are used in order to insure the transmittance of the resists and to confer a dry etching resistance. Various resins have been known as resins having an alicyclic ring, including one described by D. C. Hofer, Journal of Photopolymer Science and Technology, Vol. 9, No. 3, pages 387 - 398 (1996). In addition, it has been described, in S. Takechi et al., Journal of Photopolymer Science and Technology, Vol. 9, No. 3, pages 475 - 487 (1996) and JP-A-9-73173, that a positive working action is realized, and a high dry etching resistance, high resolution and a good adherence to substrate are obtained by using polymers or copolymers of 2-methyl-2-adamantyl methacrylate as resins for chemical amplification type resist.

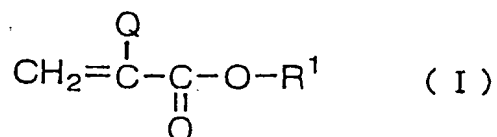
The known resins used in resists for exposure with KrF excimer laser or that with ArF excimer laser, however, did not exhibit a sufficient transmittance to a light having a wavelength of 170 nm or shorter, for example, F2 excimer laser at 157 nm. Insufficient transmittance adversely affects various performances including profile, contrast, sensitivity and so on.

The object of the present invention is to provide a chemical amplification type resist composition which is excellent in transmittance to a light having a wavelength of 170 nm or shorter and is suitably used particularly in laser lithography process with F2 excimer. The present inventors have found the fact that the transmittance to the wavelength 157 nm of F2 excimer laser can be improved by using a resin having

a polymerization unit derived from a specific monomer, as the resin constituting a resist composition. The present invention has thus been completed.

## 5 SUMMARY OF THE INVENTION

The present invention provides a chemical amplification type resist composition comprising a radiation sensitive compound; and a binder resin which is soluble in alkali by itself or becomes  
10 soluble in alkali by a chemical change caused by an action of the radiation sensitive compound after irradiation with a radiation, and has a polymerization unit derived from a monomer represented by the following formula (I):



15 wherein Q represents hydrogen, methyl or a fluoroalkyl having 1 to 4 carbon atoms; R<sup>1</sup> represents an alkyl having 1 to 14 carbon atoms which may be optionally substituted with halogen, hydroxyl or alicyclic ring, or an alicyclic or a lactone ring which may be optionally substituted with halogen, hydroxyl  
20 or alkyl; provided that at least one of Q and R<sup>1</sup> has at least one fluorine atom.

## PREFERRED EMBODIMENT OF THE INVENTION

The chemical amplification type resist composition  
25 according to the invention contains a binder resin and a radiation sensitive compound.

The binder resin contained in the chemical amplification type resist composition has a polymerization unit derived from an acrylic acid ester represented by the formula (I).

In the formula (I), at least one of Q and R<sup>1</sup> has at least one fluorine atom.

In the formula, Q represents hydrogen, methyl or a fluoroalkyl having 1 to 4 carbon atoms. The fluoroalkyl may be straight-chained or branched in the case where it has 3 or more carbon atoms. The fluoroalkyl preferably has two or more fluorine atoms. Acrylic acid esters wherein Q is a trifluoromethyl group are easily available.

R<sup>1</sup> represents an alkyl having 1 to 14 carbon atoms which may be optionally substituted with halogen, hydroxyl or alicyclic ring, or an alicyclic or a lactone ring which may be optionally substituted with halogen, hydroxyl or alkyl.

The alkyl having 1 to 14 carbon atoms which may be optionally substituted with halogen, hydroxyl or alicyclic ring may be straight-chained or branched in the case where it has 3 or more carbon atoms. Examples of the halogen as the substituent include fluorine, chlorine and bromine. Examples of the alicyclic ring as the substituent include cyclopentyl ring, cyclohexyl ring, bicyclo[2.2.1]heptyl ring, bicyclo[4.3.0]nonyl ring, bicyclo[4.4.0]decanyl ring, tricyclo[5.2.1.0<sup>2,6</sup>] decanyl ring, adamantyl ring and the like.

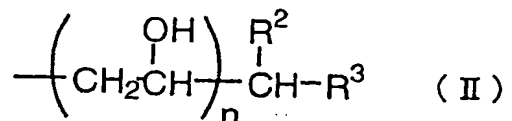
As the alkyl having 1 to 14 carbon atoms which may be optionally substituted with halogen, hydroxyl or alicyclic ring, preferred groups are fluoroalkyls having 1 to 14 carbon atoms which are substituted with at least one fluorine and which may

be optionally substituted with a hydroxyl group.

The alkyl group as a substituent on the alicyclic ring or the lactone ring is a lower alkyl group usually having about 1 to 4 carbon atoms. The alkyl group may be straight-chained or branched when it has 3 or more carbon atoms. Examples of the halogen as the substituent on the alicyclic ring or the lactone ring include fluorine, chlorine and bromine.

Examples of the alicyclic ring as R<sup>1</sup> include cyclopentyl ring, cyclohexyl ring, bicyclo[2.2.1]heptyl ring, bicyclo[4.3.0]nonyl ring, bicyclo[4.4.0]decanyl ring, tricyclo[5.2.1.0<sup>2,6</sup>]decanyl ring, adamantyl ring and the like. The lactone ring as R<sup>1</sup> include 2-oxooxetane-3-yl ring, 2-oxoxolane-3-yl ring, 2-oxooxane-3-yl ring and 2-oxepanone-3-yl ring.

When R<sup>1</sup> has at least one fluorine atom, R<sup>1</sup> is preferably a group represented by the following formula (II):



wherein R<sup>2</sup> represents hydrogen, an alkyl or a fluoroalkyl, R<sup>3</sup> represents a fluoroalkyl, the total number of carbon atoms in R<sup>2</sup> and R<sup>3</sup> is 1 to 11, and n represents 0 or 1, in the viewpoint of availability of the resin.

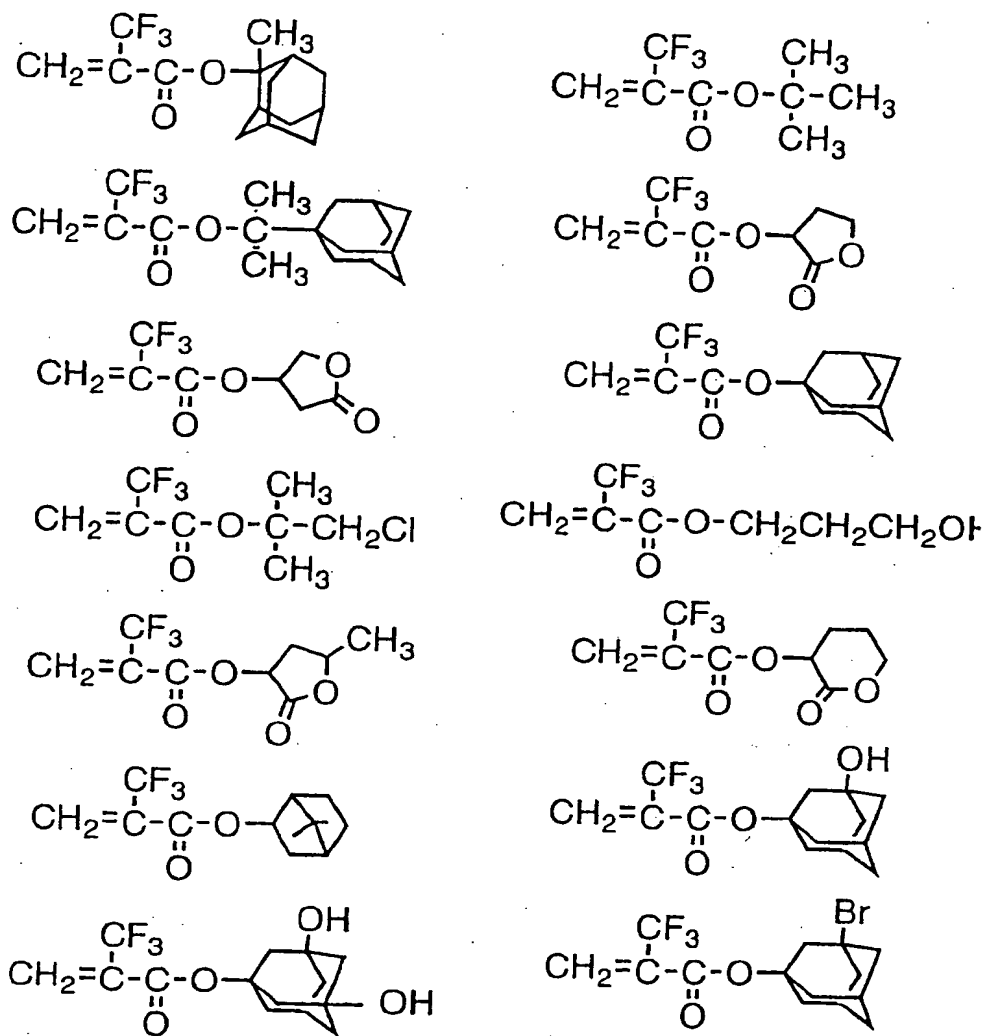
The alkyl group as R<sup>2</sup> and the fluoroalkyl group as R<sup>2</sup> or R<sup>3</sup> may be straight-chained or branched when they have 3 or more carbon atoms. The fluoroalkyl group preferably has two or more fluorine atoms. A perfluoroalkyl group may also be possible.

When R<sup>1</sup> has a hydroxyl group, the conformability of a

resin to a developer is improved as the result of increased hydrophilic property of the resin.

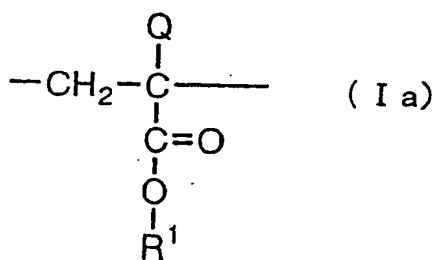
Examples of fluoroalkyl acrylate represented by the formula (I) include the following compounds:

- 5 2,2,2-trifluoroethyl acrylate,
- 2,2,2-trifluoroethyl methacrylate,
- 1-trifluoromethyl-2,2,2-trifluoroethyl acrylate,
- 1-trifluoromethyl-2,2,2-trifluoroethyl methacrylate,
- 2,2,3,3-tetrafluoropropyl methacrylate,
- 10 2,2,3,4,4,4-hexafluorobutyl methacrylate,
- 1H,1H,11H-eicosafluoroundecyl acrylate,
- 1H,1H,11H-eicosafluoroundecyl methacrylate,
- 3-(perfluoro-3-methylethyl)-2-hydroxypropyl methacrylate,
- 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl methacrylate,
- 15 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl methacrylate,
- 3-(perfluoro-7-methyloctyl)-2-hydroxypropyl methacrylate,
- 3-(perfluoroethyl)-2-hydroxypropyl methacrylate,
- 3-(perfluorobutyl)-2-hydroxypropyl methacrylate,
- 3-(perfluorohexyl)-2-hydroxypropyl methacrylate,
- 20 3-(perfluorooctyl)-2-hydroxypropyl methacrylate,
- 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl acrylate,
- 3-(perfluoro-2-methylethyl)-2-hydroxypropyl acrylate,
- 3-(perfluoro-5-methylhexyl)-2-hydroxypropyl acrylate,
- 3-(perfluoro-7-methyloctyl)-2-hydroxypropyl acrylate,
- 25 3-(perfluoroethyl)-2-hydroxypropyl acrylate,
- 3-(perfluorobutyl)-2-hydroxypropyl acrylate,
- 3-(perfluorohexyl)-2-hydroxypropyl acrylate,
- 3-(perfluorooctyl)-2-hydroxypropyl acrylate,



and the like.

A polymer unit represented by the following formula (Ia) is formed by the polymerization of a monomer represented by the formula (I):



wherein Q and R<sup>1</sup> are as defined above.



The binder resin comprised in the chemical amplification type resist composition of the present invention is soluble in alkali by itself or becomes soluble in alkali by a chemical change caused by an action of a radiation sensitive compound  
5 described below after irradiation with a radiation.

When a part of a resist film irradiated with a radiation is removed by the alkali development, such a resist is called positive type. In the positive working resist of chemical amplification type, an acid or a base generated from a radiation  
10 sensitive compound at a part irradiated with a radiation makes said part soluble in alkali by diffusing upon a heat treatment afterwards (post exposure bake) and cleaving a protective group in the resin or the like. The positive working resist of chemical amplification type includes:

15 1) those comprising a radiation sensitive compound, a binder resin soluble in alkali, and a dissolution inhibitor which has a protective group cleavable by the action of an acid or a base, and has by itself a dissolution-inhibiting ability against a binder resin soluble in alkali but loses its  
20 dissolution-inhibiting ability after said protective group is cleaved by the action of an acid or a base;

2) those comprising a radiation sensitive compound and a binder resin which has a protective group cleavable by the action of an acid or a base and is by itself insoluble or  
25 difficultly soluble in alkali but becomes soluble in alkali after said protective group is cleaved by the action of an acid or a base;  
and others.

When a binder resin is soluble in alkali and a part irradiated with a radiation is hardened and becomes insoluble in alkali, and only a part without irradiation with a radiation is removed by the alkali development, such a resist is called negative type. In the negative working resist of chemical amplification type, the binder resin is normally soluble in alkali. Such a negative working resist of chemical amplification type usually comprises, in addition to the binder resin and the radiation sensitive component, a cross-linking agent. An acid or a base generated from a radiation sensitive compound at the part irradiated with a radiation makes said part hardened and insoluble in alkali by diffusing upon a heat treatment afterwards (post exposure bake) and acting on the cross-linking agent.

Examples of the polymerization unit that confers solubility in alkali on the binder resin used in the invention (hereinafter, such a unit is referred to as alkali-soluble unit) include units having a phenol basic structure, units having a (meth)acrylic ester basic structure in which an alicyclic ring and a carboxyl group are present in the alcoholic moiety of the ester, units from unsaturated carboxylic acid and the like. Specific examples thereof include vinylphenol unit, isopropenylphenol unit, (meth)acrylic acid alicyclic ester in which a carboxyl group is present on its alicyclic ring, (meth)acrylic acid unit and the like. By introducing relatively large number of such alkali-soluble unit in the resin, the resin itself becomes soluble in alkali. The binder resin being soluble in alkali by itself as defined in the present

invention may have polymerization unit that does not confer solubility in alkali on the binder resin (hereinafter, such a unit is referred to as alkali-insoluble unit) in addition to the above alkali-soluble unit, as far as the resin as a whole is soluble in alkali. Examples of the resin having the alkali-insoluble unit include a resin having a vinylphenol unit or a isopropenylphenol unit in which the hydroxyl group is partly alkyl-esterified, a resin obtainable by copolymerization of vinylphenol or isopropenylphenol and another polymerizable unsaturated compound, a resin obtainable by copolymerization of (meth)acrylic acid alicyclic ester and (meth)acrylic acid, and the like.

Examples of resins, which are by itself insoluble or difficulty soluble in alkali but become soluble in alkali by the action of the radiation sensitive compound after irradiation of a radiation, include those having polymerization unit with a protective group which has the dissolution-inhibiting ability into the alkali developer but is cleavable by the action of an acid or a base, in addition to alkali soluble unit. The protective group which has the dissolution-inhibiting ability into the alkali developer but is cleavable by the action of an acid or a base is not particularly limited.

Examples of the protective group, which has the dissolution-inhibiting ability into the alkaline developer but is cleavable by the action of an acid, include tert-butyl, groups containing an oxygen atom connecting to a tertially carbor atom such as tert-butoxycarbonyl and tert-butoxycarbonylmethyl, acetal type groups such as

tetrahydro-2-pyranyl, tetrahydro-2-furyl, 1-ethoxyethyl, 1-(2-methylpropoxy)ethyl, 1-(2-methoxyethoxy)ethyl, 1-(2-acetoxyethoxy)ethyl, 1-[2-(1-adamantyloxy)ethoxy]ethyl and 1-[2-(1-adamantanecarbonyloxy)ethoxy]ethyl; residues of  
5 non-aromatic ring compound such as 3-oxocyclohexyl, 4-methyltetrahydro-2-pyrone-4-yl (derived from mevalonic lactone) and 2-alkyl-2-adamantyl and the like. These protective groups replace the hydrogen atom in the phenolic hydroxyl group or the carboxyl group. These protective groups  
10 can be introduced into a resin by subjecting an alkali-soluble resin having a phenolic hydroxyl group or a carboxyl group to the known protecting group-introducing reaction or by copolymerizing an unsaturated compound having such a group with another monomer.

15 Examples of the protective group which has the dissolution-inhibiting ability into the alkaline developer but is cleavable by the action of a base include alkylcarbamate or cycloalkylcarbamate groups. Examples of resins with a polymerization unit having a protective group which has the  
20 dissolution-inhibiting ability into the alkaline developer but is cleavable by the action of a base include those with a unit which has a phenol basic structure and in which phenolic hydroxyl groups are partly substituted by alkylcarbamoyloxy groups or cycloalkylcarbamoyloxy groups.

25 A polymerization unit derived from a monomer represented by the formula (I) may be an alkali-soluble unit. Alternatively, the monomer represented by the formula (I) may have a protective group which has the dissolution-inhibiting

ability into the alkaline developer but is cleavable by the action of an acid or a base. Excepting the above described cases, the binder resin of the present invention has an alkali-soluble unit or a polymerization unit having a group which becomes soluble in alkali by a chemical change caused by the action of a radiation sensitive compound after irradiation of a radiation, in addition to the polymerization unit derived from a monomer represented by the formula (I). In this case, the binder resin is produced by copolymerizing a monomer represented by the formula (I) and a monomer leading an alkali-soluble unit or a monomer that confers solubility in alkali of the resin by a chemical change caused by the action of a radiation sensitive compound after irradiation of a radiation. The copolymerization can be conducted according to a conventional process. For example, respective monomers are dissolved in a suitable solvent, then the polymerization is commenced in the presence of a polymerization initiator and the reaction proceeded towards termination.

The polymerization unit derived from the monomer represented by the formula (I) gives the binder resin containing the unit an excellent transmittance to a light having a wavelength of 170 nm or less, for example, F2 excimer laser at a wavelength of 157 nm. Therefore, it is suitable to present the polymerization unit derived from the monomer of the formula (I) in a range which allows the resin to have an excellent transmittance to a light having a wavelength of 170 nm or less as well as to be soluble in alkali or to become soluble in alkali by the action of a radiation sensitive compound after

irradiation of a radiation. Depending on the kind and type, usually the ratio of the polymerization unit derived from the monomer of the formula (I) is 10 to 100% by mole based on the total units in the resin.

5           When the binder resin contains a relatively high ratio of the alkali-soluble unit, the resin itself becomes soluble in alkali. The binder resin soluble by itself in alkali can be formulated with a dissolution inhibitor and a radiation sensitive compound to form a positive working resist, or can  
10 be formulated with a cross-linking agent and a radiation sensitive compound to form a negative working resist.

          Examples of the dissolution inhibitor used in the positive working resist in which the binder resin itself is soluble in alkali include phenol compounds in which the phenolic  
15 hydroxyl groups are protected by groups having dissolution inhibiting ability to alkaline developer but cleavable by the action of an acid or a base. Examples of the group having dissolution inhibiting ability to alkaline developer but  
20 cleavable by the action of an acid include tert-butoxycarbonyl group, which replaces hydrogen in the phenolic hydroxyl group. Examples of the dissolution inhibitor having the group having dissolution inhibiting ability to alkaline developer but  
25 cleavable by the action of an acid include 2,2-bis(4-tert-butoxycarbonyloxyphenyl)propane, bis(4-tert-butoxycarbonyloxyphenyl)sulfone, 3,5-bis(4-tert-butoxycarbonyloxyphenyl)-1,1,3-trimethyl  
indane and the like. Examples of the group having dissolution inhibiting ability to alkaline developer but cleavable by the

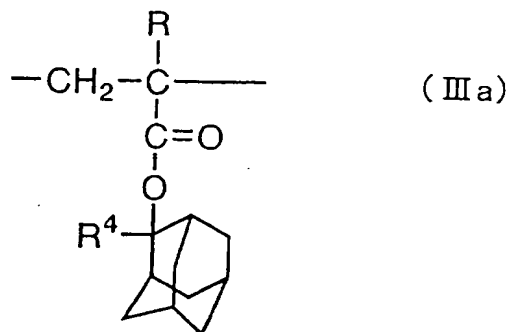
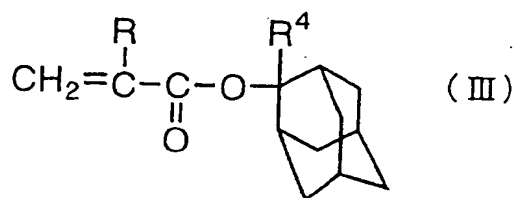
action of a base include alkylcarbamate group or cycloalkylcarbamate group and the like. Examples of dissolution inhibitor having a group cleavable by the action of a base include phenol compounds in which the phenolic hydroxyl group is replaced by an alkylcarbamoyloxy group or a cycloalkylcarbamoyloxy group. The binder component defined in this invention includes these dissolution inhibitors as well as the binder resin.

The cross-linking agent used in a negative working resist in which the binder resin itself is soluble in alkali may be anyone that causes cross-linking of the binder resin by the action of an acid or a base. Usually compounds having a methylol group or their alkyl ethers as the cross-linking agents. Specific examples thereof include methylol melamines as well as alkyl ethers thereof such as hexamethylol melamine, pentamethylol melamine, tetramethylol melamine, hexamethoxymethyl melamine, pentamethoxymethyl melamine and tetramethoxymethyl melamine; methylol benzoguanamines as well as alkyl ethers thereof such as tetramethylol benzoguanamine, tetramethoxymethyl benzoguanamine and trimethoxymethyl benzoguanamine; 2,6-bis(hydroxymethyl)-4-methylphenol as well as alkyl ethers thereof; 4-tert-butyl-2,6-bis(hydroxymethyl)phenol as well as alkyl ethers thereof; 5-ethyl-1,3-bis(hydroxymethyl)perhydro-1,3,5-triazine-2-one (common name: N-ethyldimethylol triazone) as well as alkyl ethers thereof; N,N'-dimethylolurea as well as dialkyl ethers thereof; 3,5-bis(hydroxymethyl)perhydro-1,3,5-oxadiazine-4-one (common name: dimethylol urone) as well as alkyl ethers

thereof; tetramethylol glyoxal diurein as well as tetramethyl ether thereof; and the like.

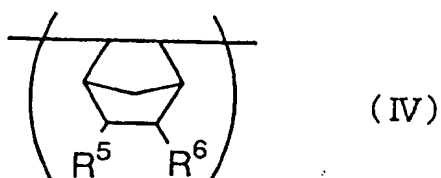
The binder resin having a unit which confers solubility in alkali on the resin by a chemical change caused by a radiation sensitive compound after irradiation of a radiation and a unit derived from the monomer of the formula (I) can be formulated with a radiation sensitive compound to form a positive working resist. Sometimes, the monomer of the formula (I) itself becomes a unit which confers solubility in alkali on the resin by a chemical change caused by a radiation sensitive compound after irradiation of a radiation. Among the polymerization unit which confers solubility in alkali on the resin by a chemical change caused by a radiation sensitive compound after irradiation of a radiation, those derived from 2-alkyl-2-adamantyl (meth)acrylates can confer an excellent resolution and dry-etching resistance on the resin. The 2-alkyl-2-adamantyl (meth)acrylates can specifically be represented by the formula (III) shown below and form polymerization units of the formula (IIIa) shown below by their polymerization.





wherein R represents hydrogen, methyl or a fluoroalkyl having 1 to 4 carbon atoms, and R<sup>4</sup> represents an alkyl. The alkyl represented by R<sup>4</sup> may have, for example, about 1 to 8 carbon atoms. Usually, it is advantageous to be straight-chained but may be branched in the case where they have 3 or more carbon atoms. Specific examples of R<sup>4</sup> include methyl, ethyl, propyl, isopropyl, butyl and the like. Since 2-alkyl-2-adamantyl group in the polymerization units of 2-alkyl-2-adamantyl (meth)acrylates represented by the formula (IIIa) is cleaved by the action of an acid, resins having these units can be used as a radiation sensitive compound in the positive working resist using an acid generating agent.

It is particularly effective for increasing the dry etching resistance that the binder resin contains an alicyclic olefin unit represented by the following formula (IV):



wherein  $R^5$  and  $R^6$ , which are same or different from each other, represent hydrogen, an alkyl having 1 to 3 carbon atoms, a hydroxyalkyl having 1 to 3 carbon atoms, carboxyl, cyano or a group  $-COOR^7$  wherein  $R^7$  is an alcohol residue, or  $R^5$  and  $R^6$  together form a carboxylic acid anhydride residue represented by  $-C(=O)OC(=O)-$ ,

and a polymerization unit of unsaturated dicarboxylic acid anhydride selected from maleic anhydride and itaconic anhydride in addition to the polymerization unit derived from the formula (I).

In the formula (IV),  $R^5$  and  $R^6$ , which are same or different from each other, may represent hydrogen, an alkyl having 1 to 3 carbon atoms, a hydroxyalkyl having 1 to 3 carbon atoms, carboxyl, cyano or a group  $-COOR^7$  wherein  $R^7$  is an alcohol residue, or  $R^5$  and  $R^6$  may together form a carboxylic acid anhydride residue represented by  $-C(=O)OC(=O)-$ . Examples of alkyls represented by  $R^5$  and  $R^6$  include methyl, ethyl, propyl and the like. Examples of hydroxyalkyls represented by  $R^5$  and  $R^6$  include hydroxymethyl, 2-hydroxyethyl and the like. Examples of alcohol residue represented by  $R^7$  include alkyl having about 1 to 8 carbon atoms which may be optionally substituted, 2-oxoxolane-3- or -4-yl and the like. Examples of possible substituent on alkyl include hydroxyl, alicyclic hydrocarbon residue and the like. Examples of carboxylic acid ester residue represented by  $-COOR^7$  include methoxycarbonyl, ethoxycarbonyl, 2-hydroxyethoxycarbonyl, tert-butoxycarbonyl, 2-oxoxolane-3-yloxycarbonyl, 2-oxoxolane-4-yloxycarbonyl, 1,1,2-trimethylpropoxycarbonyl, 1-cyclohexyl-1-

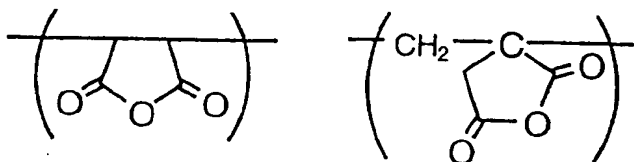
methylethoxycarbonyl, 1-(4-methylcyclohexyl)-1-methylethoxycarbonyl, 1-(1-adamantyl)-1-methylethoxycarbonyl and the like.

Examples of the monomer leading to the polymerization unit of alicyclic olefin represented by the formula (IV) include the following compounds:

- 2-norbornene,
- 2-hydroxy-5-norbornene,
- 5-norbornene-2-carboxylic acid,
- 10 methyl 5-norbornene-2-carboxylate,
- tert-butyl 5-norbornene-2-carboxylate,
- 1-cyclohexyl-1-methylethyl 5-norbornene-2-carboxylate,
- 1-(4-methylcyclohexyl)-1-methylethyl 5-norbornene-2-carboxylate,
- 15 1-(4-hydroxycyclohexyl)-1-methylethyl 5-norbornene-2-carboxylate,
- 1-methyl-1-(4-oxocyclohexyl)ethyl 5-norbornene-2-carboxylate,
- 1-(1-adamantyl)-1-methylethyl 5-norbornene-2-carboxylate,
- 20 1-methylcyclohexyl 5-norbornene-2-carboxylate,
- 2-methyl-2-adamantyl 5-norbornene-2-carboxylate,
- 2-ethyl-2-adamantyl 5-norbornene-2-carboxylate,
- 2-hydroxy-1-ethyl 5-norbornene-2-carboxylate,
- 5-norbornene-2-methanol,
- 25 5-norbornene-2,3-dicarboxylic acid anhydride and the like.

The polymerization units of unsaturated dicarboxylic acid anhydride are selected from the polymerization unit of maleic acid anhydride and the polymerization unit of itaconic

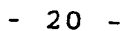
acid anhydride, and can be represented, respectively, by the formulae (V) and (VI) shown below. Examples of monomer leading to these polymerization units include maleic acid anhydride, itaconic acid anhydride and the like.

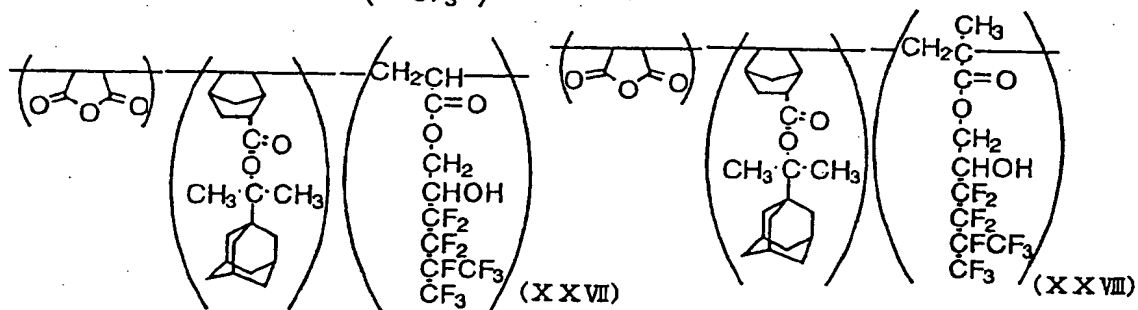
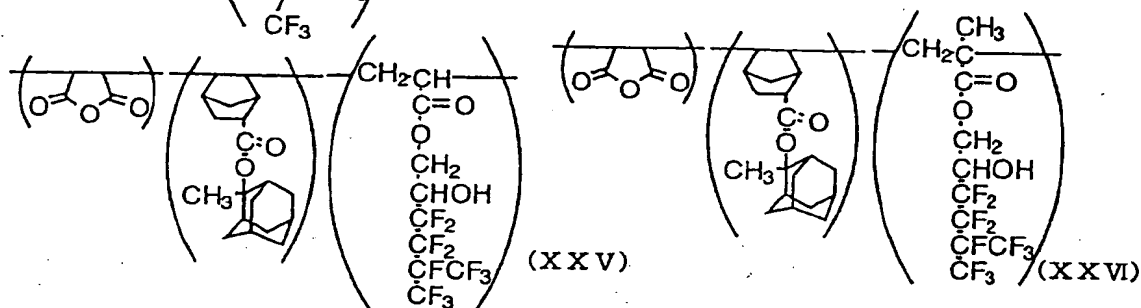
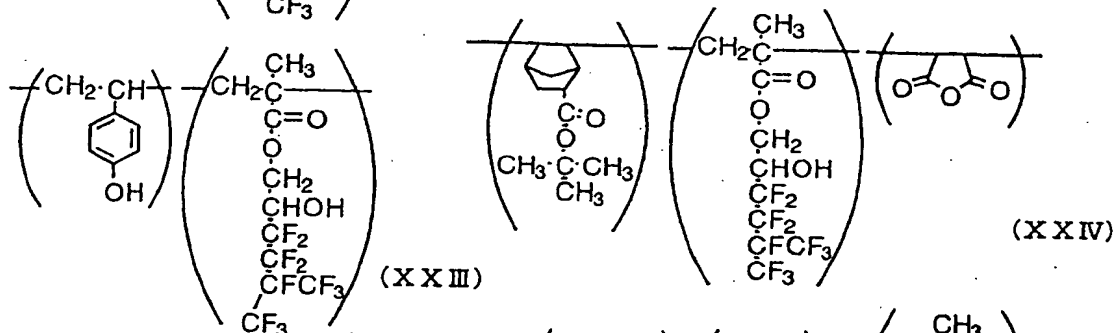
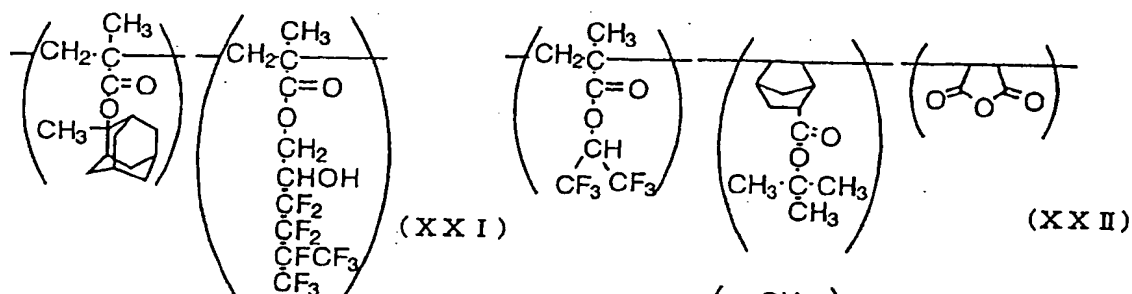


(V)

(VI)

Typical examples of binder resin, which is comprised in the resist composition of the present invention and is soluble in alkali by itself or becomes soluble in alkali by a chemical change caused by the action of a radiation sensitive compound after irradiation with a radiation, include the compounds having respective units selected from those shown by the following formulae (VII) to (XXVIII).





wherein R<sup>8</sup> represents a protective group of hydroxyl. Examples of R<sup>8</sup> include alkyl, various groups listed above as the groups cleavable by the action of an acid or a base, and the like.

- 5 In the case of a positive working resist comprising an alkali-soluble binder resin and a dissolution inhibitor having a group cleavable by the action of an acid, and in the case of a positive working resist comprising a binder resin which has a group cleavable by the action of an acid and

which is insoluble or difficultly soluble in alkali but becomes soluble in alkali after the cleavable group is cleaved, an acid generating agent which generates an acid by the action of a radiation is comprised in the positive working resist.

5 In the case of a negative working resist comprising an alkali-soluble binder resin and a cross-linking agent, usually an acid generating agent is used as a radiation sensitive compound, because many cross-linking agents cause the cross-linking reaction by the action of an acid.

10 On the other hand, in the case of a positive working resist comprising an alkali-soluble binder resin and a dissolution inhibitor having a group cleavable by the action of a base, and  
15 in the case of such a positive working resist comprising a binder resin which has a group cleavable by the action of a base, a base generating agent which generates a base by the action of a radiation is comprised in the positive working resist.

The acid generating agent as a radiation sensitive compound may be selected from various compounds which generate  
20 an acid by irradiating a radiation on a resist composition containing such a compound. Examples thereof include onium salts, halogenated alkyltriazine compounds, disulfone compounds, compounds having a diazomethanesulfonyl basic structure, sulfonic acid ester compounds and the like.  
25 Specific examples of such compounds are listed below.

Onium salts:

diphenyliodonium trifluoromethanesulfonate,  
4-methoxyphenylphenyliodonium hexafluoroantimonate,

4-methoxyphenylphenyliodonium  
 trifluoromethanesulfonate,  
 bis(4-tert-butylphenyl)iodonium tetrafluoroborate,  
 bis(4-tert-butylphenyl)iodonium hexafluorophosphate,  
 5 bis(4-tert-butylphenyl)iodonium hexafluoroantimonate,  
 bis(4-tert-butylphenyl)iodonium  
 trifluoromethanesulfonate,  
 bis(4-tert-butylphenyl)iodonium camphor sulfonate  
 triphenylsulfonium hexafluorophosphate,  
 10 triphenylsulfonium hexafluoroantimonate,  
 triphenylsulfonium trifluoromethanesulfonate,  
 4-methoxyphenyldiphenylsulfonium  
 hexafluoroantimonate,  
 4-methoxyphenyldiphenylsulfonium  
 15 trifluoromethanesulfonate,  
 p-tolyldiphenylsulfonium trifluoromethanesulfonate,  
 2,4,6-trimethylphenyldiphenylsulfonium  
 trifluoromethanesulfonate,  
 4-tert-butylphenyldiphenylsulfonium  
 20 trifluoromethanesulfonate,  
 4-phenylthiophenyldiphenylsulfonium  
 hexafluorophosphate,  
 4-phenylthiophenyldiphenylsulfonium  
 hexafluoroantimonate,  
 25 1-(2-naphthoylmethyl)thioranium hexafluoroantimonate,  
 1-(2-naphthoylmethyl)thioranium  
 trifluoromethanesulfonate,  
 4-hydroxy-1-naphthyldimethylsulfonium



hexafluoroantimonate,

4-hydroxy-1-naphthyl dimethylsulfonium  
trifluoromethanesulfonate, and the like.

Halogenated alkyl triazine compounds:

5        2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine,  
         2,4,6-tris(trichloromethyl)-1,3,5-triazine,  
         2-phenyl-4,6-bis(trichloromethyl)-1,3,5-triazine,  
         2-(4-chlorophenyl)-4,6-bis(trichloromethyl)-1,3,5-  
         triazine,

10       2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-  
         triazine,

         2-(4-methoxy-1-naphthyl)-4,6-bis(trichloromethyl)-  
         1,3,5-triazine,

         2-(benzo[d][1,3]dioxolane-5-yl)-4,6-bis(trichloro  
15 methyl)-1,3,5-triazine,

         2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-  
         triazine,

         2-(3,4,5-trimethoxystyryl)-4,6-bis(trichloromethyl)-  
         1,3,5-triazine,

20       2-(3,4-dimethoxystyryl)-4,6-bis(trichloromethyl)-  
         1,3,5-triazine,

         2-(2,4-dimethoxystyryl)-4,6-bis(trichloromethyl)-  
         1,3,5-triazine,

         2-(2-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-  
25 triazine,

         2-(4-butoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-  
         triazine,

         2-(4-pentyloxystyryl)-4,6-bis(trichloromethyl)-

1,3,5-triazine, and the like.

Disulfone compounds:

diphenyl disulfone,

di-p-tolyl disulfone,

5 phenyl p-tolyl disulfone,

phenyl p-methoxyphenyl disulfone, and the like.

Compounds having a diazomethane sulfonyl basic structure:

bis(phenylsulfonyl)diazomethane,

bis(4-chlorophenylsulfonyl)diazomethane,

10 bis(p-tolylsulfonyl)diazomethane,

bis(4-tert-butylphenylsulfonyl)diazomethane,

bis(2,4-xylylsulfonyl)diazomethane,

bis(cyclohexylsulfonyl)diazomethane,

(benzoyl)(phenylsulfonyl)diazomethane, and the like.

15 Sulfonic acid ester compounds:

1-benzoyl-1-phenylmethyl p-toluenesulfonate (common  
name: benzoin tosylate),

2-benzoyl-2-hydroxy-2-phenylethyl p-toluenesulfonate  
(common name: α-methylolbenzoin tosylate),

20 1,2,3-benzenetriyl trismethanesulfonate,

2,6-dinitrobenzyl p-toluenesulfonate,

2-nitrobenzyl p-toluenesulfonate,

4-nitrobenzyl p-toluenesulfonate,

N-(phenylsulfonyloxy)succinimide,

25 N-(trifluoromethylsulfonyloxy)succinimide,

N-(butylsulfonyloxy)succinimide,

N-(10-camphorsulfonyloxy)succinimide,

N-(trifluoromethylsulfonyloxy)phthalimide,

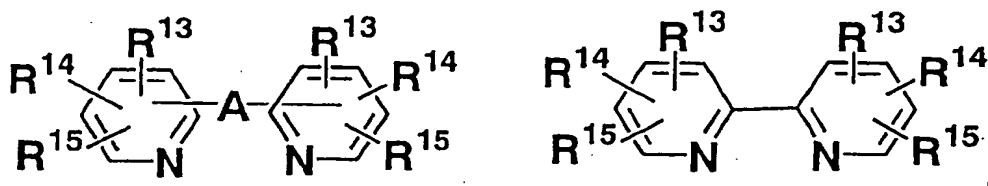
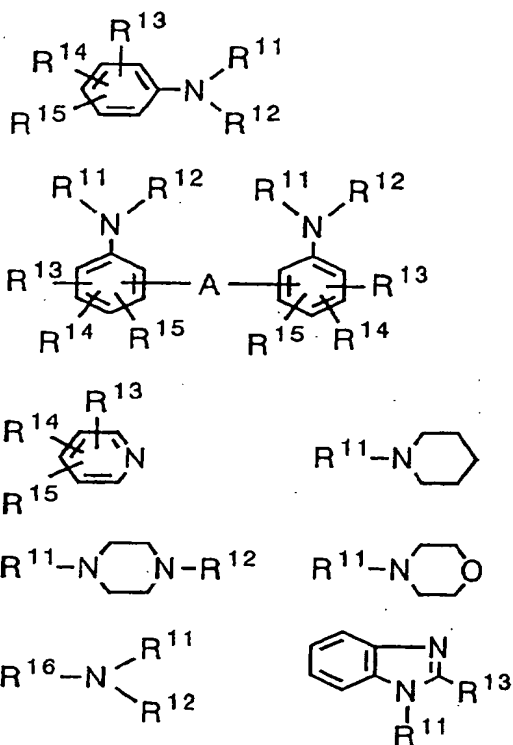
N-(trifluoromethylsulfonyloxy)-5-norbornene-2,3-dicarboxyimide,

N-(trifluoromethylsulfonyloxy)naphthalimide,

N-(10-camphorsulfonyloxy)naphthalimide, and the like.

5       The base generating agent as a radiation sensitive compound may be selected from various compounds which generate a base by irradiating a radiation on a resist composition containing such a compound. Specific examples thereof include 2-nitrobenzyl cyclohexylcarbamate, 2,6-dinitrobenzyl  
10   cyclohexylcarbamate, formanilide, triphenylsulfonium hydroxide and the like. These compounds decompose by the action of a radiation to form an amine, a hydroxyl anion or the like.

      Furthermore, it is generally known that resist  
15   compositions of chemical amplification type using an acid generating agent deteriorate in performance due to inactivation of the acid by standing after irradiation with a radiation and that such deterioration can be suppressed by adding a basic nitrogen containing organic compound, particularly an amine or  
20   the like, as a quencher. Likewise, in the present invention, when an acid generating agent is used as a radiation sensitive compound, addition of such compound is preferred. Examples of basic compound used as a quencher include compounds represented by the following formulae:



wherein  $R^{11}$  and  $R^{12}$ , which are same or different from each other, represent hydrogen, or alkyl, cycloalkyl or aryl which may be optionally substituted with a hydroxyl;  $R^{13}$ ,  $R^{14}$  and  $R^{15}$ , which are same or different from each other, represent hydrogen, or alkyl, cycloalkyl, aryl or alkoxy which may be optionally substituted with a hydroxyl;  $R^{16}$  represents alkyl or cycloalkyl which may be optionally substituted with a hydroxyl; and  $A$  represents alkylene, carbonyl, imino, disulfide, sulfide or a secondary amine. The alkyl represented by  $R^{11}$  to  $R^{16}$ , the alkoxy

represented by  $R^{13}$  to  $R^{15}$  may have about 1 to 6 carbon atoms. The cycloalkyl represented by  $R^{11}$  to  $R^{16}$  may have about 5 to 10 carbon atoms and the aryl represented by  $R^{11}$  to  $R^{15}$  may have about 6 to 10 carbon atoms. The alkylene represented by A may have about 1 to 6 carbon atoms and may be straight-chained or branched.

Furthermore, the quencher may be a hindered amine compound having a piperidine basic structure as disclosed in JP-A-11-52575.

10 The resist composition of the present invention preferably contains the binder component in a range of about 60 to 99.9% by weight and the radiation sensitive compound in a range of about 0.1 to 20% by weight, based on the total solid amount. When a dissolution inhibitor is used, the dissolution  
15 inhibitor is included in the binder component defined in this invention. The amount of the dissolution inhibitor is preferably in a range of about 5 to 40% by weight, based on the total solid amount of the resist composition. In the case of a negative working resist, preferably it contains a cross-  
20 linking agent in a range of about 1 to 30% by weight, based on the total solid amount of the resist composition. In the case of a positive working resist containing a binder resin which becomes soluble in alkali by the action of a radiation sensitive compound after irradiation of a radiation, the amount of the  
25 binder resin is preferably about 80% by weight or more, based on the total amount of the binder resin and the radiation sensitive compound. When the radiation sensitive compound is an acid generating agent and a basic compound is used as a

quencher, the amount of the quencher is preferably about 0.01 to 1% by weight, based on the total solid amount of the resist composition. The composition can further comprise, if necessary, a small amount of various additives such as photo-sensitizer, another resin, surfactant, stabilizer, dye and the like.

The resist composition of the invention is usually converted into a resist solution in which the above described components are dissolved in a solvent and applied onto a substrate such as a silicone wafer. The solvent used here may be anyone insofar as it dissolves the components, has a suitable drying rate and gives a uniform and smooth film after evaporation of the solvent, and those generally used in this field can be used. Examples of the solvent include glycol ether esters such as ethyl cellosolve acetate, methyl cellosolve acetate and propylene glycol monomethyl ether acetate; ethers such as diethylene glycol dimethyl ether; esters such as ethyl lactate, butyl acetate, amyl acetate and ethyl pyruvate; ketones such as acetone, methyl isobutyl ketone, 2-heptanone and cyclohexanone; cyclic esters such as  $\gamma$ -butyrolactone and so on. These solvents can be used independently of each other or in combination of two or more.

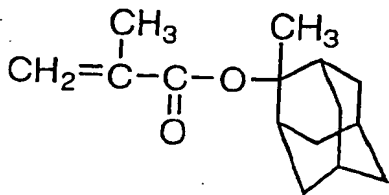
The resist film formed by applying on a substrate and drying is subjected to exposure treatment for patterning, then to heat treatment for promoting protective group-cleaving reaction or cross-linking reaction and finally developed with an alkaline developer. The alkaline developer used here may be any aqueous alkaline solutions used in this field. Widely

used developer is an aqueous solution of tetramethyl ammonium hydroxide or (2-hydroxyethyl)trimethyl ammonium hydroxide (common name: choline).

The present invention will now be described in more specific based on Examples, which by no means should be construed as a limitation upon the scope of the invention. In Examples, parts are weight based unless otherwise specified. The weight average molecular weight and the molecular weight distribution, which is weight average molecular weight/ number average molecular weight are values obtained by gel permeation chromatography using polystyrene as the standard substance.

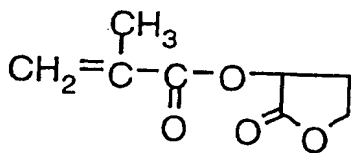
Synthetic Example 1 for Monomer (Synthesis of 2-methyl-2-adamantyl methacrylate)

Into a reaction vessel were charged 83.1 g of 2-methyl-2-adamantanol and 101 g of triethylamine, and 200 g of methyl isobutyl ketone was added thereto to form a solution. To this solution was added dropwise 78.4 g (1.5 times by mole based on 2-methyl-2-adamantanol) of methacryloyl chloride. The solution was stirred at room temperature for about 10 hours. After filtration, the organic layer was washed with 5% by weight aqueous sodium hydrogen carbonate solution and then washed twice with water. The organic layer was concentrated and distilled under reduced pressure to give 2-methyl-2-adamantyl methacrylate represented by the following formula:



Synthetic Example 2 for Monomer (Synthesis of  $\alpha$ -methacryloyloxy- $\gamma$ -butyrolactone)

5 After charging 100 g of  $\alpha$ -bromo- $\gamma$ -butyrolactone and 104.4 g (2.0 times by mole based on  $\alpha$ -bromo- $\gamma$ -butyrolactone) of methacrylic acid, 300 g of isobutyl ketone was added thereto to form a solution. To this solution was added dropwise 183.6 g (3.0 times by mole based on  $\alpha$ -bromo- $\gamma$ -butyrolactone) of triethylamine. Then, the solution was stirred at room temperature for about 10 hours. After filtration, the organic layer was washed with 5% by weight aqueous sodium hydrogen carbonate solution and then washed twice with water. The organic layer was concentrated to give  $\alpha$ -methacryloyloxy- $\gamma$ -butyrolactone represented by the following formula:



Synthetic Example for Resin (A1)

Into a 100 ml three-necked flask equipped with a magnetic stirrer, a cooler, a thermometer, a nitrogen introducer and a dropping funnel were charged 5.81 g of 2-trifluoromethyl acrylate [obtained from Kanto Chemical], 9.72 g of 2-methyl-2-adamantyl methacrylate and 10.5 g of methyl isobutyl



ketone. After replacing the air in the vessel with nitrogen, the mixture was heated to 80°C and a solution formed by dissolving 0.34 g of azobisisobutyronitrile in 10 g of methyl isobutyl ketone was added dropwise over 30 minutes. Then, the  
5 mixture was maintained for 8 hours keeping it at 80°C. After cooling the obtained reaction solution to 30°C, 7.5 g of triethylamine was added dropwise over 1 hour. Thereafter, 8.56 g of α-bromo-γ-butyrolactone was added dropwise at 35 to 45 °C over 2 hours. The reaction was continued for 8 hours keeping  
10 it at 45°C. Then the solution was filtered and the filtrate was washed 6 times with water. The washed organic layer was concentrated, combined with 2-heptanone, concentrated and added dropwise to 65% aqueous methanol. The precipitated resin was filtered and dried to give the resin A1. Amount: 14.05 g.

#### 15 Synthetic Example for Resin (A2)

Into a 100 ml three-necked flask equipped with a magnetic stirrer, a cooler, a thermometer, a nitrogen introducer and a dropping funnel were charged 15.54 g of t-butyl 5-  
20 norbornene-2-carboxylate, 7.84 g of maleic anhydride, 9.44 g of hexafluoroisopropyl methacrylate and 22 g of methyl isobutyl ketone. After replacing the air in the vessel with nitrogen, the mixture was heated to 80°C and a solution formed by dissolving 0.82 g of azobisisobutyronitrile in 11 g of methyl  
25 isobutyl ketone was added dropwise over 30 minutes. Then, the mixture was maintained for 8 hours keeping it at 80°C. Thereafter, the reaction solution was poured into a mixed solution consisting of 250 g of methanol and 100 g of water.

The precipitated resin was dissolved in propylene glycol methyl ether acetate and concentrated to give a resin solution.

Amount: 64.55 g. Solid content: 21.40%. This was referred to as the resin A2.

5

#### Synthetic Example for Resin (A3)

Into a 100 ml three-necked flask equipped with a cooler, a thermometer, a magnetic stirrer, a nitrogen introducer and a dropping funnel were charged 8.59 g of 2-methyladamantyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (hereinafter, may be  
10 expressed as "NB-2Mad"), 2.94 g of maleic anhydride (hereinafter, may be expressed as "MA"), 5.97 g of 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl acrylate (hereinafter, may be expressed as "TFMC700HAA") and 10 g of  
15 4-methyl-2-pentanone. The air in the vessel was replaced with nitrogen. After heating the mixture to 80°C, a 0.31 g of azobisisobutyronitrile dissolved in 7 g of 4-methyl-2-pentanone was added dropwise over 30 minutes. Then, the mixture was maintained for 8 hours keeping it at 80°C. After  
20 cooling, the reaction solution was poured into 300 ml of methanol and the precipitated resin was collected by filtration. Vacuum drying at 40°C for 8 hours gave 10.2 g of a resin. Weight average molecular weight (Mw) converted to polystyrene: 6,400. This was referred to as the resin A3.

25

#### Synthetic Example for Resins (A4, A5 and X1)

According to similar procedures to the procedure in Synthetic Example for Resin (A3), resins listed in the following

Table were obtained:

	Monomer composition charged	Mw
Synthetic Example		
	for Resin A4: NB-TB/MA/TFMC70HAA=40/40/20	6,100
5 Synthetic Example		
	for Resin A5: NB-2Mad/MA/TFMC70HAA=45/45/10	5,500
Synthetic Example		
	for Resin X1: NB-TB/MA=50/50	5,400
	NB-TB: 2-methylpropyl bicyclo[2.2.1]hept-5-ene-	
10 2-carboxylate		

#### Synthetic Example for Resin (A6)

Into a 100 ml three-necked flask equipped with a cooler, a thermometer, a magnetic stirrer, a nitrogen introducer and a dropping funnel were charged 9.43 g of 2-adamantylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (NB-AdTB), 2.94 g of maleic anhydride, 5.97 g of 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl acrylate and 10 g of 4-methyl-2-pentanone. The air in the vessel was replaced with nitrogen. After heating the mixture to 80°C, 0.31 g of azobisisobutyronitrile dissolved in 7 g of 4-methyl-2-pentanone was added dropwise over 30 minutes. Then, the mixture was maintained for 8 hours keeping it at 80°C. After cooling, the reaction solution was poured into 300 ml of hexane and the precipitated resin was collected by filtration. Vacuum drying at 40°C for 8 hours gave 7.3 g of a resin. Weight average molecular weight (Mw) converted to polystyrene: 10,900. This was referred to as the resin A6.

#### Synthetic Example for Resin (A7)

The procedure in Synthetic Example for Resin A6 was repeated except that the molar ratio of the charged monomers was changed to NB-AdTB/MA/TFMC7OHMA = 40/40/20 to give a resin.

- 5 Weight average molecular weight (Mw) converted to polystyrene: 16,700. This was referred to as the resin A7.

#### Synthetic Example for Resin (A8)

- Into a 100 ml three-necked flask equipped with a cooler,  
10 a thermometer, a magnetic stirrer, a nitrogen introducer and a dropping funnel were charged 7.03 g of 2-adamantyl methacrylate (hereinafter, may be expressed as "2MadMA"), 12.37 g of (perfluoro-3-methylbutyl)-2-hydroxypropyl acrylate and 10 g of 4-methyl-2-pentanone. The air in the vessel was  
15 replaced with nitrogen. After heating the mixture to 80°C, 0.25 g of azobisisobutyronitrile dissolved in 7 g of 4-methyl-2-pentanone was added dropwise over 30 minutes. Then, the mixture was maintained for 8 hours keeping it at 80°C. After cooling, the reaction solution was poured into 300 ml of hexane  
20 and the precipitated resin was collected by filtration. Vacuum drying at 40°C for 8 hours gave 10.5g of a resin. Weight average molecular weight (Mw) converted to polystyrene: 24,000. This was referred to as the resin A8.

#### 25 Synthetic Example for Resin (X2)

After charging 2-methyl-2-adamantyl methacrylate and  $\alpha$ -methacryloyloxy- $\gamma$ -butyrolactone in a molar ratio of 5 : 5 (15.0 g/11.7 g), methyl ethyl ketone in twice by weight of total

monomers was added to form a solution. Then, azobisisobutyronitrile in 2% by mole based on the amount of total monomers was added as an initiator and the solution was heated to 80°C for about 8 hours. Thereafter, purification was effected by pouring the reaction solution into a large quantity of heptane and this operation was carried out 3 times in total. As the result, a copolymer having a weight average molecular weight of about 10,000 was obtained. This was referred to as the resin X2.

10

Examples 1 to 8 and Comparative Examples 1 and 2

Components listed below were mixed and filtered through a fluorine resin filter having a pore diameter of 0.2  $\mu\text{m}$  to give resist solutions.

15

Resin

10 parts

Acid generating agent:

p-tolyldiphenylsulfonium trifluoromethanesulfonate

0.2 part

20

("MDS-205", obtained from Midori Chemical)

Quencher: 2,6-diisopropyl aniline

0.015 part

Solvent: propylene glycol monomethyl ether acetate

100 parts

25

The resist solutions prepared as above were coated on silicon wafers which had been treated with hexamethylsilazane at 23°C for 20 seconds so that the film thickness after drying was 0.1  $\mu\text{m}$ . The prebake was carried out under conditions of

120°C for 60 seconds on a direct hot plate. The wafers having a resist film formed in such manner were exposed with a simplified F2 excimer laser exposure apparatus ["VUVES-4500" obtained from Lithotec Japan] through an open frame, changing stepwise the amount of exposure. After exposure, the wafers were subjected to post-exposure bake (PEB) at a temperature of 120°C for 60 seconds on a hot plate and then to paddle development in 2.38% aqueous tetramethylammonium hydroxide solution for 60 seconds. Wafers obtained after development were assessed by visual observation and the minimum exposure at which the resist film dropped (film-dropping sensitivity) was determined to give the results shown in Table 1.

On other hand, each of the resist solutions prepared as above and solutions obtained by dissolving each of the resins alone in propylene glycol monomethyl ether acetate was coated on a magnesium fluoride wafer so that the film thickness after drying was 0.1  $\mu\text{m}$ . The prebake was carried out under conditions of 120°C for 60 seconds on a direct hot plate to form resist films. The resist films formed in such manner were assessed for transmittance at a wavelength of 157 nm using the transmittance-measurement ability of the simplified F2 excimer laser exposure apparatus used above to give the results shown in Table 1.

Table 1

Resin Film-dropping sensitivity			Transmittance	
			Resin only	Resist
Example 1	A1	2 mJ/cm <sup>2</sup>	35%	35%
Example 2	A2	5 mJ/cm <sup>2</sup>	36%	33%
Example 3	A3	3 mJ/cm <sup>2</sup>	32%	30%
Example 4	A4	4.5 mJ/cm <sup>2</sup>	38%	36%
Example 5	A5	4 mJ/cm <sup>2</sup>	28%	26%
Example 6	A6	2.5 mJ/cm <sup>2</sup>	33%	31%
Example 7	A7	3.5 mJ/cm <sup>2</sup>	30%	30%
Example 8	A8	1 mJ/cm <sup>2</sup>	44%	43%
Comparative				
Example 1	X1	8 mJ/cm <sup>2</sup>	26%	25%
Comparative				
Example 1	X2	3 mJ/cm <sup>2</sup>	25%	25%

## Synthetic Example for Resin (A9)

Into a 100 ml flask equipped with a magnetic stirrer,  
 a cooler, a thermometer, a nitrogen introducer and a dropping  
 funnel were charged 10.31 g of 3-perfluoro-3-methylbutyl)-  
 2-hydroxypropyl methacrylate [obtained from Daikin Kaseihin  
 Hanbail], 17.63 g of p-t-butoxystyrene and 31 g of methyl  
 isobutyl ketone. After replacing the air in the vessel with  
 nitrogen, the mixture was heated to 80°C and a solution formed  
 by dissolving 0.82 g of azobisisobutyronitrile in 11 g of methyl  
 isobutyl ketone was added dropwise over 30 minutes. Then, the  
 mixture was maintained for 8 hours keeping it at 80°C. Then  
 the solution was poured into a mixed solution consisting of 250  
 g of methanol and 100 g of water. The precipitated resin was

dissolved in methyl isobutyl ketone and concentrated to give 57.6 g of a resin solution. To this resin solution were added 62.8 g of methyl isobutyl ketone, 3.0 g of p-toluenesulfonic acid and 9.7 g of water and heated at 70°C for 15 hours. The  
5 obtained reaction solution was washed 5 times with water and concentrated. Then, 300 g of propylene glycol methyl ether acetate was added and concentration was continued to give a resin solution. Amount: 65.3 g. Solid content: 27.21%.  
Weight average molecular weight: 14,900. This was referred to  
10 as the resin A9.

#### Synthetic Example for Resin (A10)

Into a 200 ml flask equipped with a magnetic stirrer, a cooler, a thermometer, a nitrogen introducer and a dropping  
15 funnel was charged 26.81 g of methyl isobutyl ketone. After replacing the air in the vessel with nitrogen, the mixture was heated to 84°C and a solution formed separately by dissolving 9.89 g of 3-perfluoro-3-methylbutyl)-2-hydroxypropyl  
methacrylate [obtained from Daikin Kaseihin Hanbail], 16.92 g  
20 of p-t-butoxystyrene and 1.97 g of azobisisobutyronitrile in 26.81 g of methyl isobutyl ketone was added dropwise over 1 hour. Then, the mixture was maintained for 8 hours keeping it at 84  
°C. The reaction solution was poured into a mixed solution consisting of 247.23 g of methanol and 123.61 g of water over  
25 30 minutes. The obtained resin was dissolved in methyl isobutyl ketone and concentrated to give 67.03 g of a resin solution.

To this resin solution were added 93.52 g of methyl



isobutyl ketone, 3.49 g of p-toluenesulfonic acid and 11.26 g of water and heated at 70°C for 15 hours. The obtained reaction solution was washed 5 times with water, concentrated and then added dropwise to 446.88 g of n-heptane over 30 minutes. The  
5 obtained resin was filtered and vacuum-dried to give the product resin. Amount: 17.07 g. Weight average molecular weight: 4,400. This was referred to as the resin A10.

Resin X3: a resin obtained by protecting hydroxyl groups in  
10 poly(p-vinylphenol) (commercial name: "VP-2500", manufactured by Nippon Soda) with isopropyl group at an average protection rate of 20%.

#### Examples 9 and 10 and Comparative Example 3

15 Components, listed below, were mixed and filtered through a fluorine resin filter having a pore diameter of 0.2  $\mu\text{m}$  to give resist solutions.

Resin (as solid content)	10 parts
20 Cross-linking agent: hexamethoxymethyl melamine	0.5 part
Acid generating agent: N-(isopropylsulfonyloxy)succinimide	1.1 part
Quencher: 1,3-di(4-pyridyl)propane	0.0125 part
25 Solvent (including solvent derived from the resin solution): propylene glycol monomethyl ether acetate	100 parts

An organic reflection-preventing membrane having a thickness of 600 angstrom, which was prepared by applying a composition "DUV-42" for organic reflection-preventing membrane, manufactured by Brewer, and baking under conditions of 215°C for 60 seconds, was formed on a silicon wafer. The resist solution obtained above was applied on said wafer with a spin coater so that the film thickness after drying was 0.523  $\mu\text{m}$ . After applying the resist solution, the wafer was pre-baked on a direct hotplate under conditions of 100°C for 60 seconds. The wafer having a resist film formed thereon was irradiated with a KrF excimer stepper ["NSR-2205 EX12B", manufactured by Nikon, NA = 0.55,  $\sigma$  = 0.8] through a line-and-space pattern, changing stepwise the exposure amount. The exposed wafer was subjected to post-exposure baking (PEB) on a hot plate under conditions of 105°C for 60 seconds. Then the wafer was subjected to paddle development with 2.38% by weight aqueous tetramethyl ammonium hydroxide solution for 60 seconds. The developed line-and-space pattern was observed by a scanning electron microscope and assessed for the effective sensitivity and the resolution by the following methods:

Effective sensitivity: This is expressed in the minimum amount of exposure which gave 1 : 1 line-and-space pattern of 0.20  $\mu\text{m}$ .

Resolution : This is expressed in the minimum size which gave line-and-space pattern spitted at the exposure amount of the effective sensitivity.

The resist solutions prepared as above and solutions obtained by dissolving the resin alone in propylene glycol monomethyl ether acetate were coated on magnesium fluoride wafers so that the film thickness after drying was 0.1  $\mu\text{m}$ . The prebake was carried out under conditions of 100°C for 60 seconds on a direct hot plate to form resist films. The resist films formed in such manner were assessed for transmittance at a wavelength of 157 nm using the transmittance-measurement ability of the simplified F2 excimer laser exposure apparatus ("VUVES-4500", manufactured by Lithotec Japan) to give the results shown in Table 2.

Table 2

	Resin	Transmittance		Effective sensitivity (KrF)	Resolution (KrF)
		Resin only	Resist		
Example 9	A9	40%	40%	18 mJ/cm <sup>2</sup>	0.16 $\mu\text{m}$
Example 10	A10	39%	38%	90 mJ/cm <sup>2</sup>	0.15 $\mu\text{m}$
Comparative Example 3	X3	27%	27%	27 mJ/cm <sup>2</sup>	0.16 $\mu\text{m}$

#### 15 Synthetic Example for Resin (A11)

Into a four-necked flask equipped with a magnetic stirrer, a nitrogen introducer, a Dimroth condenser, a thermometer and a dropping funnel were charged 9.37 g of 2-methyl-2-adamantyl methacrylate, 9.44 g of 1-trifluoromethyl-2,2,2-trifluoroethyl methacrylate [obtained from Tokyo Kasei Industries], 0.263 g of azobisisobutyronitrile and 40.9 g of methyl isobutyl ketone. The air in the vessel was replaced with nitrogen. Then, flowing

nitrogen stream in the system, the mixture was heated to 80 °C with an oil bath and maintained the temperature for about 7 hours. After cooling, the reaction solution was poured into 1 dm<sup>3</sup> of methanol with stirring. After continuing the stirring for 30 minutes, the solution was filtered to give 25.8 g of white powders. The white powders were dried under reduced pressure at 60°C for about 6 hours to give 8.4 g of a resin. Yield: 45%. Weight average molecular weight: 10,200. This was referred to as the resin A11.

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#### Examples 11 and Comparative Example 4

Components listed below were mixed and filtered through a fluorine resin filter having a pore diameter of 0.2 µm to give resist solutions.

15

Resin (as solid content)	10 parts
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Acid generating agent:

p-tolyldiphenylsulfonium trifluoromethanesulfonate

("MDS-205", obtained from Midori Chemicals) 0.2 part

20 Quencher: dicyclohexylmethylamine	0.015 part
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Solvent:	100 parts
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Example: 2-heptanone

Comparative Example: propylene glycol monomethyl ether acetate/γ-butyrolactone (95/5)

25

An organic reflection-preventing membrane having a thickness of 1,600 angstrom, which was prepared by applying a composition "DUV-30J-14" for organic reflection-preventing

membrane, manufactured by Brewer, and baking under conditions of 215°C for 60 seconds, was formed on a silicon wafer. The resist solution obtained above was applied on said wafer with a spin coater so that the film thickness after drying was 0.39  $\mu\text{m}$ . After applying the resist solution, the wafer was pre-baked on a direct hotplate under conditions of 120°C for 60 seconds. The wafer having a resist film formed thereon was irradiated with an ArF eximer stepper ["NSR ArF", manufactured by Nikon, NA = 0.55,  $\sigma$  = 0.6] through a line-and-space pattern, changing stepwise the exposure amount. The exposed wafer was subjected to post-exposure baking (PEB) on a hot plate under conditions of 120°C for 60 seconds. Then the wafer was subjected to paddle development with 2.38% by weight aqueous tetramethyl ammonium hydroxide solution for 60 seconds. The developed line-and-space pattern was observed by a scanning electron microscope and the effective sensitivity and the resolution were assessed by the following methods:

Effective sensitivity: This is expressed in the minimum amount of exposure which gave 1 : 1 line-and-space pattern of 0.18  $\mu\text{m}$ .

Resolution : This is expressed in the minimum size which gave line-and-space pattern spitted at the exposure amount of the effective sensitivity.

The resist solutions prepared as above and solutions obtained by dissolving the resin alone in propylene glycol monomethyl ether acetate were coated on magnesium fluoride

wafers so that the film thickness after drying was 0.1  $\mu\text{m}$ . The prebake was carried out under conditions of 120°C for 60 seconds on a direct hot plate to form resist films. The resist films formed in such manner were assessed for transmittance at a wavelength of 157 nm using the transmittance-measurement ability of the simplified F2 excimer laser exposure apparatus ("VUVES-4500", manufactured by Lithotec Japan) to give the results shown in Table 3.

Table 3

	Resin	Transmittance		Effective sensitivity	Resolution
		Resin only	Resist		
Example 11	A11	30%	30%	42 mJ/cm <sup>2</sup>	0.16 $\mu\text{m}$
Comparative Example 4	X2	25%	25%	36 mJ/cm <sup>2</sup>	0.16 $\mu\text{m}$

#### Synthetic Example for Resin (A12)

Into a 100 ml flask equipped with a stirrer, a cooler, a thermometer and a nitrogen introducer were charged 9.73 g of p-acetoxystyrene, 2.56 g of t-butyl acrylate, 7.96 g of 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl methacrylate [obtained from Daikin Industries Co. Ltd.], and 13.51 g of isopropyl alcohol. After replacing the air in the vessel with nitrogen, the mixture was heated to 80°C and a solution formed by dissolving 0.41 g of azobisisobutyronitrile in 6.75 g of isopropyl alcohol was added dropwise over 30 minutes. Then, the mixture was maintained for 6 hours keeping it at 80°C. Thereafter, the reaction mixture was poured into a mixed solution of methanol and water to precipitate the resin which

was then filtered and dried to give 15.69 g of resin.

Into a 100 ml flask equipped with a stirrer, a cooler, a thermometer and a nitrogen introducer were charged 15.69 g of the resin obtained above, 1.57 g of 4-dimethylaminopyridine and 47.07 g of methanol, and the mixture was kept for 15 hours under reflux. Then, after cooling, the mixture was neutralized with 0.93 g of glacial acetic acid. The neutralized mixture was charged to 784.50 g of water to precipitate the resin which was then filtered to obtain a resin crystal. The resin crystal was dissolved in acetone and the obtained solution was charged to water to precipitate the resin which was then filtered to obtain a resin crystal, and this operation is repeated three times. Then, the crystal thus obtained was dried to obtain 12.59 g of resin. The weight average molecular weight was 37,000 and the molecular weight distribution was 3.72. Hereinafter, this resin is expressed as "Resin A 12".

#### Synthetic Example for Resin (A13)

Into a 100 ml flask equipped with a stirrer, a cooler, a thermometer and a nitrogen introducer were charged 9.73 g of p-acetoxystyrene, 4.69 g of 2-methyl-2-adamantyl methacrylate, 7.96 g of 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl methacrylate [obtained from Daikin Industries Co. Ltd.], and 13.92 g of isopropyl alcohol. After replacing the air in the vessel with nitrogen, the mixture was heated to 80°C and a solution formed by dissolving 0.41 g of azobisisobutyronitrile in 7.46 g of isopropyl alcohol was added dropwise over 30 minutes. Then, the mixture was maintained for 6 hours keeping it at 80

°C. Thereafter, the reaction mixture was poured into a mixed solution of methanol and water to precipitate the resin which was then filtered and dried to give 22.08 g of resin.

Into a 300 ml flask equipped with a stirrer, a cooler,  
5 a thermometer and a nitrogen introducer were charged 22.08 g of the resin obtained above, 2.21 g of 4-dimethylaminopyridine and 110 g of methanol, and the mixture was kept for 15 hours under reflux. Then, after cooling, the mixture was neutralized with 2.21 g of glacial acetic acid. The neutralized mixture  
10 was charged to 2000 g of water to precipitate the resin which was then filtered to obtain a resin crystal. The resin crystal was dissolved in acetone and the obtained solution was charged to water to precipitate the resin which was then filtered to obtain a resin crystal, and this operation is repeated three  
15 times. Then, the crystal thus obtained was dried to obtain 11.51 g of resin. The weight average molecular weight was 30,900 and the molecular weight distribution was 1.99. Hereinafter, this resin is expressed as "Resin A 13".

#### 20 Resin X4

TSM-4, a terpolymer of t-butylacrylate, styrene and p-hydroxystyrene manufactured by Maruzen Petrochemical Co., Ltd., is hereinafter expressed as "Resin X4". The  
polymerization ratio of t-butylacrylate, styrene and p-  
25 hydroxystyrene in Resin X4 was measured with a nuclear magnetic resonance ( $^{13}\text{C}$ -NMR) spectrometer, and it is about 20/20/60.

Synthetic Example for Resin (X5)



(1) Into a flask were charged 39.7 g (0.245 mol) of p-acetoxystyrene, 24.6 g (0.105 mol) of 2-methyl-2-adamantyl methacrylate and 128.6 g of isopropyl alcohol. After replacing the air in the vessel with nitrogen, the mixture was heated to 75°C and a solution formed by dissolving 4.84 g (0.021 mol) of dimethyl 2,2-azobis(2-methylpropionate) in 9.7 g of isopropyl alcohol was added dropwise. Then, the mixture was maintained for 30 minutes at 75°C, and for 11 hours under reflux.

Thereafter, the reaction mixture was diluted with acetone and the obtained solution was charged to heptane to precipitate the resin which was then filtered. The resin obtained by the filtration was dried to give 54.1 g of crystal of copolymer of p-acetoxystyrene and 2-methyl-2-adamantyl methacrylate.

(2) Into a flask were charged 53.2 g of the copolymer of p-acetoxystyrene and 2-methyl-2-adamantyl methacrylate, 5.3 g (0.043 mol) of 4-dimethylaminopyridine and 159.5 g of methanol, and the mixture was kept for 20 hours under reflux. Then, after cooling, the mixture was neutralized with 3.92 g (0.065 mol) of glacial acetic acid. The neutralized mixture was charged to water to precipitate the resin which was then filtered to obtain a resin crystal. The resin crystal was dissolved in acetone and the obtained solution was charged to water to precipitate the resin which was then filtered to obtain a resin crystal, and this operation is repeated three times. Then, the crystal thus obtained was dried to give 41.2 g of crystal of copolymer of p-hydroxystyrene and 2-methyl-2-adamantyl methacrylate. The weight average molecular weight was 8,100 and the molecular weight distribution was 1.68. The

polymerization ratio of p-acetoxystyrene and 2-methyl-2-adamantyl methacrylate was measured with a nuclear magnetic resonance ( $^{13}\text{C}$ -NMR) spectrometer, and it is about 70/30. Hereinafter, this resin is expressed as "Resin X5".

5

#### Synthetic Example for Resin (X6)

- (1) Into a flask were charged 45.4 g (0.28 mol) of p-acetoxystyrene, 16.4 g (0.07 mol) of 2-methyl-2-adamantyl methacrylate and 123.6 g of isopropyl alcohol. After replacing the air in the vessel with nitrogen, the mixture was heated to 75°C and a solution formed by dissolving 4.84 g (0.021 mol) of dimethyl 2,2-azobis(2-methylpropionate) in 9.7 g of isopropyl alcohol was added dropwise. Then, the mixture was maintained for 30 minutes at 75°C, and for 11 hours under reflux.
- 15 Thereafter, the reaction mixture was diluted with acetone and the obtained solution was charged to heptane to precipitate the resin which was then filtered. The resin obtained by the filtration was dried to give 54.2 g of crystal of copolymer of p-acetoxystyrene and 2-methyl-2-adamantyl methacrylate.
- 20 (2) Into a flask were charged 53.0 g of the copolymer of p-acetoxystyrene and 2-methyl-2-adamantyl methacrylate, 5.3 g (0.043 mol) of 4-dimethylaminopyridine and 159.0 g of methanol, and the mixture was kept for 20 hours under reflux. Then, after cooling, the mixture was neutralized with 3.13 g (0.052 mol)
- 25 of glacial acetic acid. The neutralized mixture was charged to water to precipitate the resin which was then filtered to obtain a resin crystal. The resin crystal was dissolved in acetone and the obtained solution was charged to water to

precipitate the resin which was then filtered to obtain a resin crystal, and this operation is repeated three times. Then, the crystal thus obtained was dried to give 37.8 g of crystal of copolymer of p-hydroxystyrene and 2-methyl-2-adamantyl methacrylate. The weight average molecular weight was about 7,900 and the molecular weight distribution was 1.72. The polymerization ratio of p-acetoxystyrene and 2-methyl-2-adamantyl methacrylate was measured with a nuclear magnetic resonance (<sup>13</sup>C-NMR) spectrometer, and it is about 80/20. Hereinafter, this resin is expressed as "Resin X6".

#### Example 12 and Comparative Example 5

Components listed below were mixed and filtered through a fluorine resin filter having a pore diameter of 0.2 μm to give resist solutions.

Resin

10 parts

Acid generating agent:

bis(4-tert-butylphenyl)iodonium camphor sulfonate

0.52 part

Quencher: tripropanol amine

0.052 part

Solvent: ethyl lactate

100 parts

#### Example 13 and Comparative Example 6

Components listed below were mixed and filtered through a fluorine resin filter having a pore diameter of 0.2 μm to give resist solutions.

Resin	10 parts
Acid generating agent:	
bis(4-tert-butylphenyl)iodonium camphor sulfonate	0.52 part
5 Quencher: 2,6-diisopropyl aniline	0.052 part
Solvent: methyl amyl ketone	100 parts

The resist solutions prepared as above were coated on silicon wafers which had been treated with hexamethylsilazane at 23°C for 20 seconds so that the film thickness after drying was 0.1  $\mu\text{m}$ . The prebake was carried out under conditions of 130°C for 60 seconds on a direct hot plate. The wafers having a resist film formed in such manner were exposed with a simplified F2 excimer laser exposure apparatus ["VUVES-4500" obtained from Lithotec Japan] through an open frame, changing stepwise the amount of exposure. After exposure, the wafers were subjected to post-exposure bake (PEB) at a temperature of 140°C for 60 seconds on a hot plate and then to paddle development in 2.38% aqueous tetramethylammonium hydroxide solution for 60 seconds. Wafers obtained after development were assessed by visual observation and the minimum exposure at which the resist film dropped (film-dropping sensitivity) was determined to give the results shown in Table 4.

On other hand, each of the resist solutions prepared as above and solutions obtained by dissolving each of the resins alone in propylene glycol monomethyl ether acetate was coated on a magnesium fluoride wafer so that the film thickness after drying was 0.1  $\mu\text{m}$ . The prebake was carried out under conditions

of 130°C for 60 seconds on a direct hot plate to form resist films. The resist films formed in such manner were assessed for transmittance at a wavelength of 157 nm using a vacuum ultra-violet spectrometer (VUV-200, manufactured by JASCO Corporation) to give the results shown in Table 4.

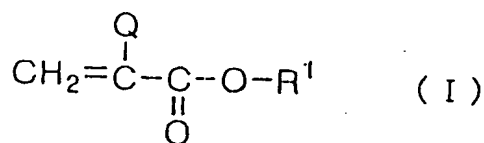
Table 4

Resin Film-dropping			Transmittance	
		sensitivity	Resin only	Resist
Example 12	A12	2.5 mJ/cm <sup>2</sup>	30%	31%
Example 13	A13	0.5 mJ/cm <sup>2</sup>	27%	27%
Comparative				
Example 5	X4	2 mJ/cm <sup>2</sup>	24%	25%
Comparative				
Example 6	X5/X6=1	3 mJ/cm <sup>2</sup>	21%	22%

The resist composition of the present invention exhibits a high transmittance in a light exposure using a light source having a wavelength of 170 nm or less, for example, F2 excimer laser at 157 nm. The resist composition also exhibits a high resolution in KrF or ArF light exposure and has a sufficient contrast. Therefore, the resist composition can exhibit an excellent performance as a resist of chemical amplification type using a light source having a wavelength of 170 nm or less.

CLAIMS

1. A chemical amplification type resist composition comprising a radiation sensitive compound; and
- 5 a binder resin which is soluble in alkali by itself or becomes soluble in alkali by a chemical change caused by the action of the radiation sensitive compound after irradiation, and has a polymerization unit derived from a monomer of formula (I):

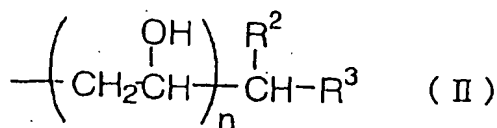


10

wherein Q represents hydrogen, methyl or a fluoroalkyl having 1 to 4 carbon atoms; R<sup>1</sup> represents an alkyl having 1 to 14 carbon atoms which may be optionally substituted with halogen, hydroxyl or alicyclic ring, or an alicyclic or lactone ring which may be optionally substituted with halogen, hydroxyl or alkyl; provided that at

15 least one of Q and R<sup>1</sup> has at least one fluorine atom.

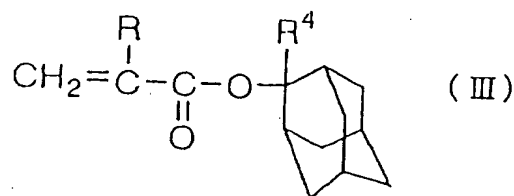
2. A composition according to claim 1 wherein Q is a trifluoromethyl group.
3. A composition according to claim 1 to 2 wherein R<sup>1</sup> is a fluoroalkyl having 1 to 14 carbon atoms which is substituted with at least one fluorine and which may be optionally substituted with a hydroxyl group.
- 20 4. A composition according to claim 3 wherein the fluoroalkyl having 1 to 14 carbon atoms which is substituted with at least one fluorine and which may be optionally substituted with a hydroxyl group is of formula (II):



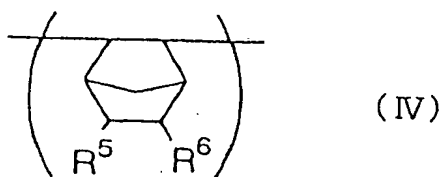
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wherein R<sup>2</sup> represents hydrogen, an alkyl or a fluoroalkyl, R<sup>3</sup> represents a fluoroalkyl, the total number of carbon atoms in R<sup>2</sup> and R<sup>3</sup> is 1 to 11, and n represents 0 or 1.

5. A composition according to any one of claims 1 to 4 which is of positive type and wherein the radiation sensitive compound is an active agent which generates an acid or a base by the action of radiation.
6. A composition according to claim 5, wherein the binder resin has a protective group cleavable by the action of an acid or a base, and is insoluble or difficultly soluble in alkali but becomes soluble in alkali after said protective group is cleaved by the action of an acid or a base.
7. A composition according to claim 5 or 6, wherein the binder resin has a unit derived from a 2-alkyl-2-adamantyl (meth)acrylate of formula (III):



- 15 wherein R represents hydrogen, methyl or a fluoroalkyl having 1 to 4 carbon atoms, and R<sup>4</sup> represents an alkyl, in addition to the polymerization unit derived from the monomer of formula (I); and the radiation sensitive compound is an acid generating agent which generates an acid by the action of radiation.
- 20 8. A composition according to any one of claims 5 to 7, wherein the binder resin has an alicyclic olefin unit of formula (IV):



- 25 wherein R<sup>5</sup> and R<sup>6</sup>, which are the same as or different from each other, represent hydrogen, an alkyl having 1 to 3 carbon atoms, a hydroxyalkyl having 1 to 3 carbon atoms, carboxyl, cyano or a group -COOR<sup>7</sup> wherein R<sup>7</sup> is an alcohol residue, or R<sup>5</sup> and R<sup>6</sup> together form a carboxylic acid anhydride residue -C(=O)OC(=O)-,
- 30

and an unsaturated dicarboxylic acid anhydride unit selected from maleic anhydride and itaconic anhydride, in addition to the polymerization unit derived from the monomer of formula (I).

9. A composition according to any one of claims 1 to 4 wherein the binder resin  
5 is soluble in alkali, and which is of negative type and comprises a cross-linking agent in addition to the binder resin and the radiation sensitive component.
10. A composition according to claim 1 substantially as hereinbefore described in any one of Examples 1 to 13.





INVESTOR IN PEOPLE

Application No: GB 0027168.4  
Claims searched: 1-10

Examiner: Carol Davies  
Date of search: 20 December 2000

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.R): G2C (CRPC, CRM)

Int CI (Ed.7): G03F 7/004, 7/038, 7/039

Other: ONLINE: EPODOC, JAPIO, WPI

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	JP 100239846 A (FUJI) See WPI & PAJ Abstracts	1, 5 & 6 at least
X	US 5665527 (IBM) See whole document, especially Example in column 6.	
A	US 5660969 (FUJITSU) See column 1 line 46 to column 2 line 33.	

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

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A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
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